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**KUMMER SANITARY LANDFILL  
SUPPLEMENTAL ALTERNATIVES EVALUATION  
GROUNDWATER EXTRACTION AND TREATMENT**

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## **1.0    INTRODUCTION**

This Supplemental Alternatives Evaluation is being prepared to provide information regarding a fourth alternative for the third operable unit at the Kummer Sanitary Landfill (Site). The alternative under consideration deals strictly with the treatment technology for extracted groundwater at the Site. This technology would be proposed in the event that bioremediation is determined not to be feasible for groundwater treatment at the Site.

## **2.0    BACKGROUND**

Remedial actions at the Site have been broken into three operable units:

Operable Unit 1	Northern Township Municipal Water System
Operable Unit 2	Source control (capping) of the landfill
Operable Unit 3	Contaminated groundwater management

Operable Units 1 and 2 are being addressed separately by the regulatory agencies and the Potentially Responsible Parties (PRPs) and are not included in this evaluation. The third operable unit was evaluated in the Site Feasibility Study (FS) prepared for the Minnesota Pollution Control Agency (MPCA) in July 1990 and in the Record of Decision (ROD) prepared by US EPA and signed on September 29, 1990.

The groundwater remedial action objectives stated in the FS are to:

1. Provide a safe drinking water supply for down-gradient residents.
2. Prevent significant impacts on surface water quality.

The first objective is being met with the anticipated completion of connections by this summer, by operable unit one. The second objective, if applicable, is to be met by installation of the landfill cap and the groundwater extraction and treatment system.

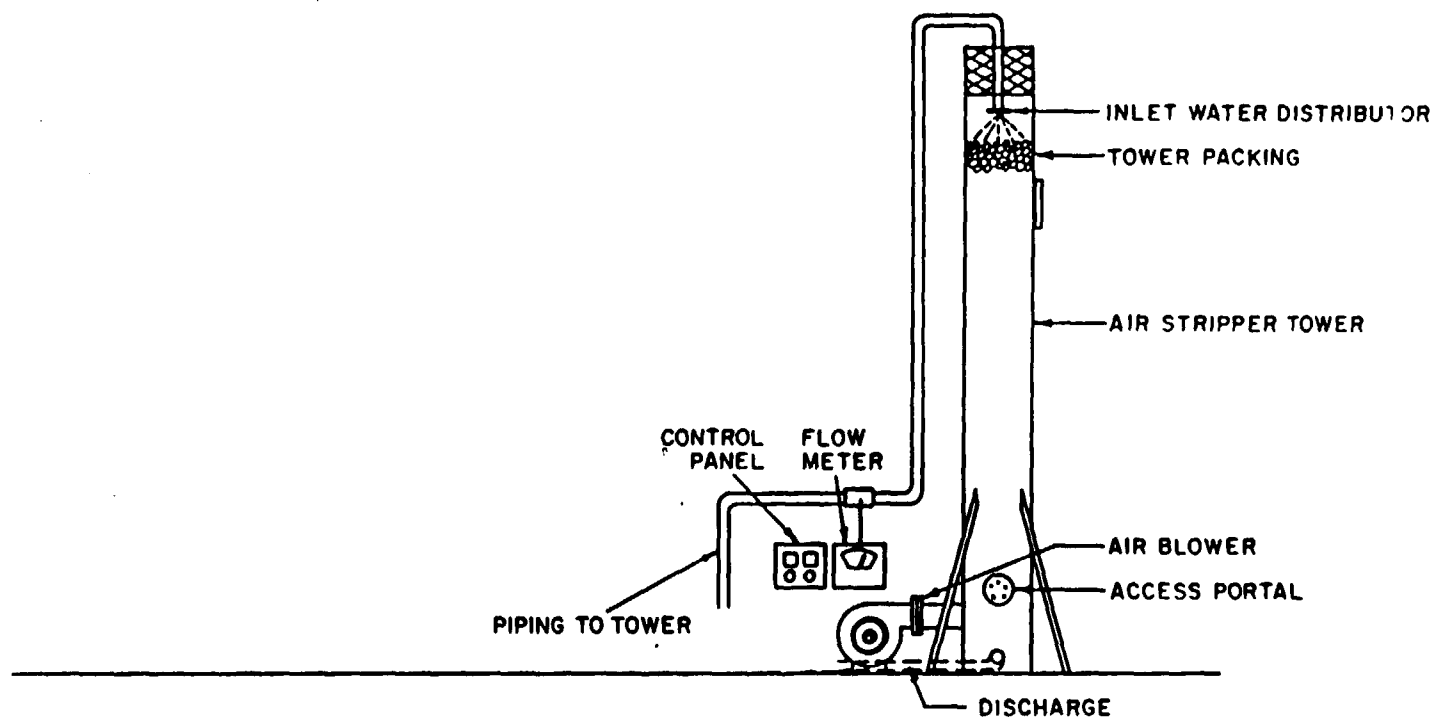
The groundwater contamination consists of low level volatile organic compound (VOC) contamination as well as some inorganic parameters that exceed primary and secondary drinking water criteria at some locations sampled. The selected remedy in the ROD consisted of groundwater extraction, lime softening to remove inorganic contaminants and advanced

oxidation process (AOP) followed by a granular activated carbon polish for VOC removal. Based on recent evaluation of the selected remedy by the PRPs for the Site, an additional alternative is being proposed for consideration.

### **3.0 PROPOSED ALTERNATIVE**

The proposed alternative groundwater treatment consists of groundwater extraction as selected in the ROD, followed by pH adjustment and coagulation/flocculation for inorganics removal and air stripping for organics removal. The treated groundwater recharge alternative selected in the ROD would be retained if the city discharge system is unavailable. In order to address potential air emission concerns stated in the FS, a screening evaluation of air stripper exhaust gases was performed which shows that VOC emissions will be well below  $10^{-5}$  exposure levels and in conformance with OSWER Directive 9355.0-28. The Directive was provided by the MPCA as the criteria document for ambient impacts at the Site. Groundwater extraction, inorganics treatment and recharge are described in the FS and the ROD and will not be repeated here.

The treatment technology being proposed for VOC removal is air stripping. Figure 1 illustrates the schematic diagram of the proposed treatment system. In order to verify adequate removal of VOCs from groundwater and insignificant ambient impact, a conservative estimate of influent VOC concentrations was utilized based on the highest concentrations of



NOT TO SCALE

figure 1  
AIR STRIPPER  
*Kummer Landfill*

CRA

the VOC parameters at the Site. Following is a list of the concentrations utilized for the purpose of this estimate and a comparative list of the influent concentrations used in the FS:

<u>Compound</u>	<u>Concentration for Evaluation (µg/l)</u>	<u>Concentration From FS (µg/l)</u>
Benzene	6.0	4.0
Tetrachloroethene	12.0	-
Trichloroethene	6.8	-
Trans-1,2-Dichloroethene	35.0	5.0
Vinyl Chloride	94.0	33.0

### 3.1 GROUNDWATER TREATMENT

Based on the influent concentrations evaluated, a preliminary design of an air stripper has been identified. Table 1 presents the conceptual specifications for the air stripper and includes the specifications presented in Table 3.6 of the FS. Based on the conceptual design evaluated, treated effluent will be below Maximum Contaminant Levels (MCLs) for the VOCs identified. Table 2 lists predicted effluent and exhaust gas VOC concentrations based on the proposed air stripper design. Actual concentrations will be less than these estimates based on anticipated actual influent concentrations.

**TABLE 1**  
**AIR STRIPPER SPECIFICATIONS**  
**KUMMER SANITARY LANDFILL, BEMIDJI, MINNESOTA**

<u>Parameter</u>	<u>Proposed Design</u>	<u>FS Design</u>
Hydraulic Capacity	100 gpm	100 gpm
Diameter	30 inches	24 inches
Packing Height	13 feet	8 feet
Air Flowrate	700 cfm	400 cfm
Air : Water Ratio	50:1	30:1



TABLE 2

**AIR STRIPPER EFFLUENT AND  
EXHAUST GAS COMPOUND CONCENTRATIONS  
KUMMER SANITARY LANDFILL, BEMIDJI, MINNESOTA**

Liquid Inflow Rate 100 gpm  
Air Inflow Rate 700 cfm

<u>Compounds</u>	<u>Mole Weight</u> (gm/mole)	<u>Influent</u> <u>Liquid Conc.</u> (ug/l)	<u>Effluent</u> <u>Liquid Conc.</u> (ug/l)	<u>Off-Gas</u> <u>Mass of Contaminant</u> (#/day)	<u>Off-Gas</u> <u>Mass of Contaminant</u> (#/c.f.)	<u>Off-Gas</u> <u>Concentration</u> <u>Contaminant</u> (PPM)
Tetrachloroethene (PCE)	166	12.0	0.33	1.40E-02	1.39E-08	0.0312
Trichloroethene (TCE)	131	6.8	0.16	7.97E-03	7.91E-09	0.0225
Trans-1,2-Dichloroethene (tDCE)	97	35.0	0.64	4.13E-02	4.09E-08	0.1574
Vinyl Chloride	63	94.0	1	1.12E-01	1.11E-07	0.6558
Benzene	78	6.0	0.18	6.99E-03	6.93E-09	0.0331
		153.8	2.31	1.82E-01	1.80E-07	0.9000

### **3.2 EXHAUST AIR TREATMENT**

A detailed evaluation of potential air emissions from the air stripper exhaust will be conducted during the remedial design phase of the program. Estimated air emissions will be evaluated in conjunction with stack height and acceptable risk levels to confirm no significant ambient impact. Based upon verbal discussions with USEPA and MPCA, catalytic incineration of the exhaust gases was also evaluated and determined to be feasible, if required. A paper discussing the feasibility of catalytic incineration of halogenated organic chemicals is attached as Appendix A. However, the scope and costs were not included because the estimated concentrations of VOCs in the exhaust gases are well below any adverse risk levels as utilized by USEPA and MPCA as demonstrated on Table 3.

### **4.0 PROPOSED ALTERNATIVE ANALYSIS**

The proposed alternative of coagulation/flocculation followed by air stripping are evaluated based on the nine criteria used for evaluating remedial alternatives.

**TABLE 3**  
**AIR STRIPPER EXHAUST GAS**  
**IMPACT/COMPLIANCE EVALUATION**  
**KUMMER SANITARY LANDFILL**

1. Nonattainment considerations - None.
2. Attainment considerations -

VOC air emissions are "de minimis" with respect to PSD (0.033 TPY vs 40.0), "minor" under the CAAA (0.033 TPY vs 10), and not significant with respect to OSWER Directive 9355.0-28 (0.0076 lb/hr vs 3.0).

The following table contains individual emission estimates:

<u>Compound</u>	<u>Emissions (lb/hr)</u>	<u>Emissions (TPY)</u>
PCE	$5.84 \times 10^{-4}$	$2.56 \times 10^{-3}$
TCE	$3.32 \times 10^{-4}$	$1.46 \times 10^{-3}$
TDCE	$1.72 \times 10^{-3}$	$7.52 \times 10^{-3}$
Vinyl Chloride	$4.65 \times 10^{-3}$	$2.04 \times 10^{-2}$
Benzene	$2.91 \times 10^{-4}$	$1.28 \times 10^{-3}$
<b>TOTAL</b>	<b>0.0076</b>	<b>0.033</b>

3. Ambient Impact Analysis

A. Risk - based compounds

The individual and aggregate maximum ground level concentrations, at the nearest property boundary, are  $60 \times 7700 \times$  less the RsD safe levels.

Stack Parameters:  $H = 30' = 9.2M$     $x = 100M$     $d = 0.76M$   
 $T = \text{ambient } (293^\circ K)$     $V_s = 0.72 \text{ mps}$

Screening Model: SCREEN (USEPA)

<u>Compound</u>	<u>Maximum 1 hr conc.</u>	<u>(mg/m<sup>3</sup>) Maximum Am. Conc.<sup>1</sup></u>	<u>RsD Safe Levels<sup>2</sup></u>	<u>Fractional Impact<sup>3</sup></u>
PCE	0.11	0.0028	21.0	0.00013
TCE	0.062	0.0016	7.7	0.00021
Vinyl Chloride	0.87	0.022	1.4	0.0157
Benzene	0.054	0.0014	1.2	0.0012
<b>Aggregate Total</b>				<b>0.017 vs 1.0</b>

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1 Average: 25% if 1 hour value  
2 From USEPA (56 FR 7232, 2/21/91)  
3 (Ann. Conc.) + (Safe Level)

**TABLE 3 (Cont'd)**  
**AIR STRIPPER EXHAUST GAS**  
**IMPACT/COMPLIANCE EVALUATION**  
**KUMMER SANITARY LANDFILL**

**B. Toxic Air Compounds**

The ground level concentration, at the nearest property boundary, is 36,000 x less than PEL - based on safe levels.

<u>Compound</u>	<u>Maximum 1 hr conc.</u>	<u>8 hr Conc.<sup>4</sup></u>	<u>PEL - based Safe Level<sup>5</sup></u>	<u>Fractional Impact</u>
TDCE	0.32	0.22	7930	0.000028 vs 1.0

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<sup>4</sup> USEPA: 70% of 1 hr value

<sup>5</sup> At 1% of PEL.

\*\*\* SCREEN-1.1 MODEL RUN \*\*\*  
\*\*\* VERSION DATED 88300 \*\*\*

Kummer, Mr L/F: GW air stripper (vinyl chloride)

SIMPLE TERRAIN INPUTS:

SOURCE TYPE = POINT  
EMISSION RATE (G/S) = .5880E-03  
STACK HEIGHT (M) = 9.20  
STK IN=IDE DIAM (M) = .76  
STK EXIT VELOCITY (M/S) = .72  
STK GAS EXIT TEMP (K) = 293.00  
AMBIENT AIR TEMP (K) = 293.00  
RECEPTOR HEIGHT (M) = .00  
IOPT (1=URB,2=RUR) = 2  
BUILDING HEIGHT (M) = .00  
MIN HORIZ BLDG DIM (M) = .00  
MAX HORIZ BLDG DIM (M) = .00

BUOY. FLUX = .00 M\*\*4/S\*\*3; MOM. FLUX = .07 M\*\*4/S\*\*2.

\*\*\* FULL METEOROLOGY \*\*\*

\*\*\*\*\*  
\*\*\* SCREEN AUTOMATED DISTANCES \*\*\*  
\*\*\*\*\*

\*\*\* TERRAIN HEIGHT OF 0. M ABOVE STACK BASE USED FOR FOLLOWING DISTANCES \*\*\*

DIST (M)	CONC (UG/M**3)	STAB	U10M (M/S)	USTK (M/S)	MIX HT (M)	PLUME HT (M)	SIGMA Y (M)	SIGMA Z (M)	DWASH
100.	.8673	3	1.0	1.0	320.0	9.7	12.5	7.5	NO
200.	.7781	5	1.0	1.0	5000.0	9.7	11.6	6.3	NO
300.	.6854	5	1.0	1.0	5000.0	9.7	16.9	8.7	NO
400.	.7080	6	1.0	1.0	5000.0	9.7	14.6	7.1	NO
500.	.6383	6	1.0	1.0	5000.0	9.7	18.0	8.4	NO
600.	.5516	6	1.0	1.0	5000.0	9.7	21.2	9.7	NO
700.	.4722	6	1.0	1.0	5000.0	9.7	24.5	10.9	NO
800.	.4071	6	1.0	1.0	5000.0	9.7	27.6	12.0	NO
900.	.3540	6	1.0	1.0	5000.0	9.7	30.8	13.0	NO
1000.	.3104	6	1.0	1.0	5000.0	9.7	33.9	14.0	NO

MAXIMUM 1-HR CONCENTRATION AT OR BEYOND 100. M:

100.	.8673	3	1.0	1.0	320.0	9.7	12.5	7.5	NO
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DWASH= MEANS NO CALC MADE (CONC = 0.0)  
DWASH=NO MEANS NO BUILDING DOWNWASH USED  
DWASH=HS MEANS HUBER-SHYOER DOWNWASH USED  
DWASH=SS MEANS SCHULMAN-SCIRE DOWNWASH USED  
DWASH=NA MEANS DOWNWASH NOT APPLICABLE, X<3\*LB

\*\*\*\*\*  
\*\*\* SUMMARY OF SCREEN MODEL RESULTS \*\*\*  
\*\*\*\*\*

CALCULATION PROCEDURE	MAX CONC (UG/M**3)	DIST TO MAX (M)	TERRAIN HT (M)
SIMPLE TERRAIN	.8673	100.	0.

#### **4.1 OVERALL PROTECTION OF HUMAN HEALTH AND THE ENVIRONMENT**

The proposed alternative reduces the risks associated with groundwater contamination by pumping and treating contaminated groundwater in a comparable manner as achieved in the selected remedy and meets the intent of the criteria in the ROD.

#### **4.2 ARARs COMPLIANCE**

The proposed alternative for the Site meets or exceeds ARARs as discussed in Section X(B) of the ROD. It is expected to meet MCLs within 10 years of treatment, which is equivalent to the selected alternative in the ROD.

#### **4.3 LONG TERM EFFECTIVENESS AND PERFORMANCE**

The proposed alternative utilizes the same groundwater pumping component and a comparable treatment component as the selected alternative. Elimination of the groundwater contaminants achieves the same degree of long-term effectiveness and permanence as the selected alternative.

#### **4.4 REDUCTION OF TOXICITY, MOBILITY OR VOLUME THROUGH TREATMENT**

The proposed alternative achieves the same degree of reduction of toxicity and mobility as the selected remedy and achieves a better reduction of volume because the inorganics treatment generates less sludge requiring land disposal and the air stripping achieves MCLs without the generation of contaminated carbon.

#### **4.5 SHORT TERM EFFECTIVENESS**

The proposed alternative achieves the same degree of short term effectiveness as the selected alternative.

#### **4.6 IMPLEMENTABILITY**

The proposed alternative is equally implementable as the selected alternative and is being utilized at numerous sites in Region V including the following four National Priorities List Sites in Minnesota: Lehiller/Mankato, Waite Park Wells, Twin Cities Army Ammunition Plant and General Mills/Henkel Corporation.

#### **4.7 COST**

The proposed alternative is more cost effective than the selected alternative for both capital and operation/maintenance costs. Following is a summary cost comparison. Detailed cost estimates are shown in Tables 4 and 5. Costs for groundwater extraction, inorganics treatment, advanced oxidation and groundwater recharge employ the figures from the FS.

	<b><u>Proposed Alternative</u></b>	<b><u>Selected Alternative</u></b>
Capital Cost	\$1,000,000	\$1,370,000
Annual O & M Cost	\$400,000	\$512,000
Present Worth Cost (10%)	\$4,770,000	\$6,200,000



**TABLE 4**  
**DETAILED REMEDIAL COST ESTIMATE**  
**AIR STRIPPING WITH CATALYTIC INCINERATION**  
**KUMMER SANITARY LANDFILL**

<u>Component</u>	<u>Capital Cost</u>
Packed tower with blower	\$ 18,000
Controls & Instrumentation	12,000
Piping & Valves	2,000
Electrical	3,000
Site work	3,000
Foundation and clearwell	35,000
Building	30,000
Land Acquisition	3,000
Miscellaneous	<u>5,000</u>
Sub-Total Construction Costs	111,000
Contingency @ 20%	22,000
Engineering @ 15%	<u>17,000</u>
<b>TOTAL CAPITAL COST:</b>	<b>\$ 150,000</b>
 <u>Operating Costs</u>	 <u>Annual Cost</u>
Electrical Power	\$ 7,000
Labor	50,000
Maintenance Materials	10,000
Monitoring	30,000
Insurance, taxes & licenses	<u>5,000</u>
Sub-Total Annual O & M Costs	102,000
Contingency @ 25%	<u>26,000</u>
<b>TOTAL ANNUAL O &amp; M</b>	<b>\$ 128,000</b>

**TABLE 5**  
**REMEDIAL COST ESTIMATE**  
**GROUNDWATER EXTRACTION AND TREATMENT**  
**KUMMER SANITARY LANDFILL**

<u>Component</u>	<u>Proposed Alternative</u>	<u>Selected Remedy</u>
Groundwater Collection	\$ 300,000	\$ 300,000
Inorganics Removal	320,000	400,000
Organics Removal	150,000	440,000
Groundwater Recharge	230,000	230,000
Present Worth O & M <sup>1</sup>	<u>3,770,000</u>	<u>4,830,000</u>
<b>TOTAL COST:</b>	<b><u>\$ 4,770,000</u></b>	<b><u>\$ 6,200,000</u></b>

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<sup>1</sup>Based on 30 year operating life discounted at 10% (9.43).

#### **4.8 STATE ACCEPTANCE**

The MPCA concurred with the selected alternative from the ROD. The proposed alternative meets equivalent levels of the nine criteria and is a better alternative because it generates less sludge and is more cost effective.

#### **4.9 COMMUNITY ACCEPTANCE**

The proposed alternative is comparable or superior to the selected remedy and should therefore be acceptable to the community. Two of the concerns raised during the public comment period were cost effectiveness and sludge generation. As previously stated, the proposed alternative is better than the selected alternative in both of those areas.

**APPENDIX A**  
**CATALYTIC DESTRUCTION**  
**OF**  
**HAZARDOUS HALOGENATED**  
**ORGANIC CHEMICALS**

# **CATALYTIC DESTRUCTION OF HAZARDOUS HALOGENATED ORGANIC CHEMICALS**

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Air & Waste Management Association  
82nd Annual Meeting & Exposition  
June 25 — 30, 1989  
Anaheim, California**



products or by-products as phosgene, chlorine ( $\text{Cl}_2$ ), vinyl chloride monomer, etc.; collection or trapping of gas samples for separate GC analysis; scrubbing the gas with prepared analytical solutions for subsequent titration, ion chromatography, or other analytical procedures; and determination and continuous analysis for hydrocarbon and/or halogenated hydrocarbons by a heated flame ionization analyzer (Beckman 400) and for  $\text{CO}_2$  and CO by appropriate Beckman non-dispersive infrared analyzers. The flame ionization detector (FID) was calibrated for each halohydrocarbon with the feed stream by-passing the reactor on the assumption that the published vapor pressure of the halohydrocarbon was correct and that saturation and mixing were proper. This assumption was tested, and corrected if necessary, by the  $\text{CO}_2$  and CO analysis of the product gas at a condition when complete destruction of the compound was occurring, based on NDIR,  $\text{CO}_2$ , and CO analyzers. If necessary, confirmatory analysis was done by gas detector tubes and/or supplemental GC analysis.

The quartz test reactor is shown in Figure 2. The feed blend is preheated by the furnace and the reactor effluent as it flows past the catalyst bed in an annular section; flow then reverses and continues through the catalyst monolith or the bed of catalyst extrudate or granules. The catalyst bed section was normally 7/8" diameter and 1' long; the fixed beds of extruded particles were supported by a short section of uncatalyzed 400 cells/in<sup>2</sup> ceramic (cordierite) monolith. The catalyst bed length and/or gas flow rate (normally 2.5 liters (STP) per minute) were adjusted as needed to obtain space velocities other than the usual 15,000 hr<sup>-1</sup> GHSV (STP).

#### Normal test procedure

After the feed blend had been analyzed through the reactor bypass, the catalyst was heated to 400°C in the flowing feed blend. If feed destruction was less than 90% at that condition, the temperature was increased to achieve 90% destruction. The temperature was then cooled down at a rate of about 4°C/minute, while the degree of destruction was continuously monitored. Because of the reactor design, there were normally only small temperature gradients (< 5°C) across the catalyst bed. For consistency, inlet temperatures have been used for all of the data presented here.

#### Catalyst

The proprietary halohydrocarbon destruction catalyst (HDC) was prepared in the form of a coated monolith and also as extruded (1/16" diameter x 1/16" long) pellets. The monolithic support was the 400 cells/in<sup>2</sup> Corning cordierite ceramic (square cells, 8mil wall thickness) used in conventional automotive catalytic converters.

#### Products of catalytic destruction

Complete catalytic destruction of the feed halogenated organics minimizes the possibilities of production of hazardous products of incomplete combustion (PICs) such as carbon monoxide (CO). It is also important that sufficient hydrogen be present in the feed, as organic matter and/or water vapor, to minimize production of chlorine gas

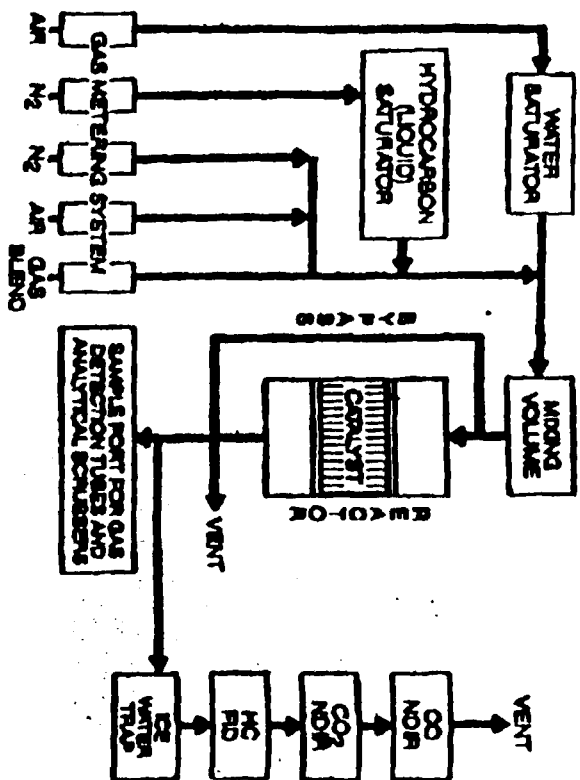


Figure 1. Schematic diagram of laboratory activity test apparatus.

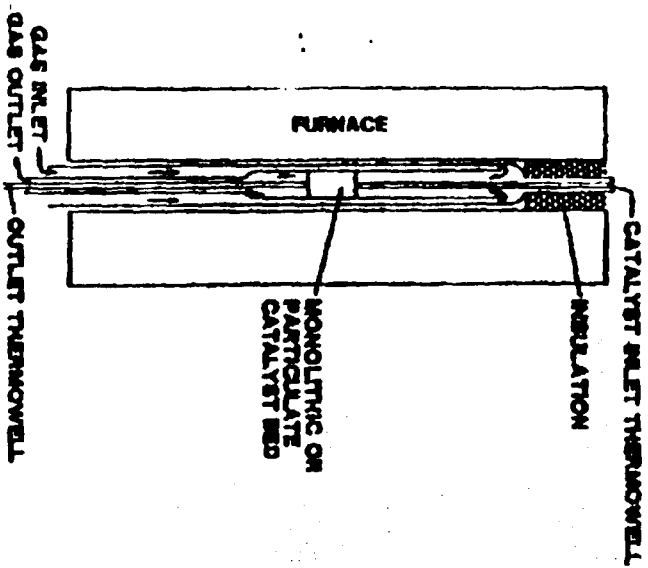


Figure 2. Diagram of engine activity test reactor.

(Cl<sub>2</sub>) rather than the desired hydrogen chloride (HCl). In the occasional measurements of HCl and Cl<sub>2</sub> yield, the Cl<sub>2</sub> was always below 20 volume ppm in the effluent or less than 6 percent of the total inorganic chloride produced.

## RESULTS

### Relevant prior studies

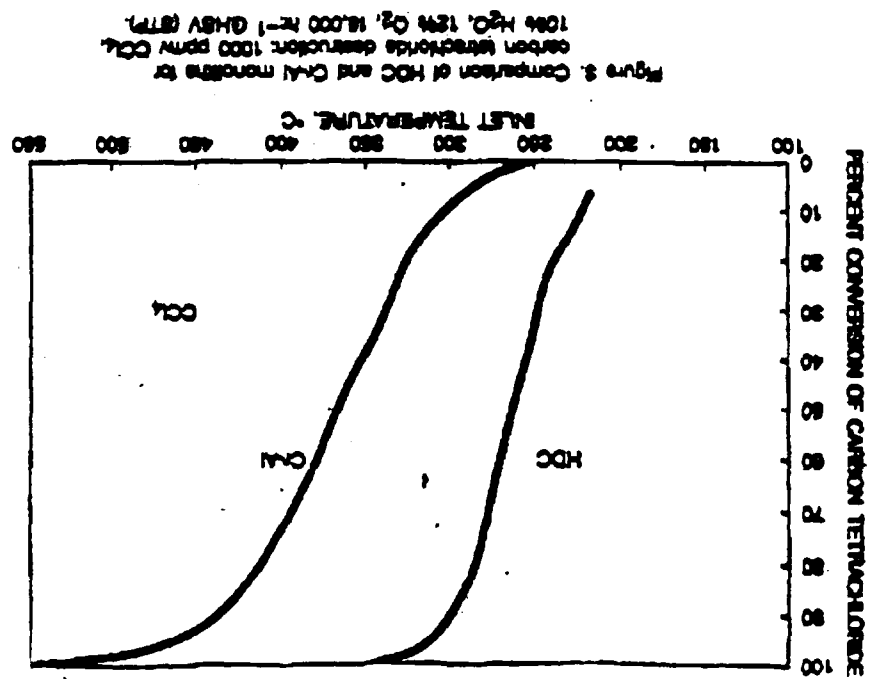
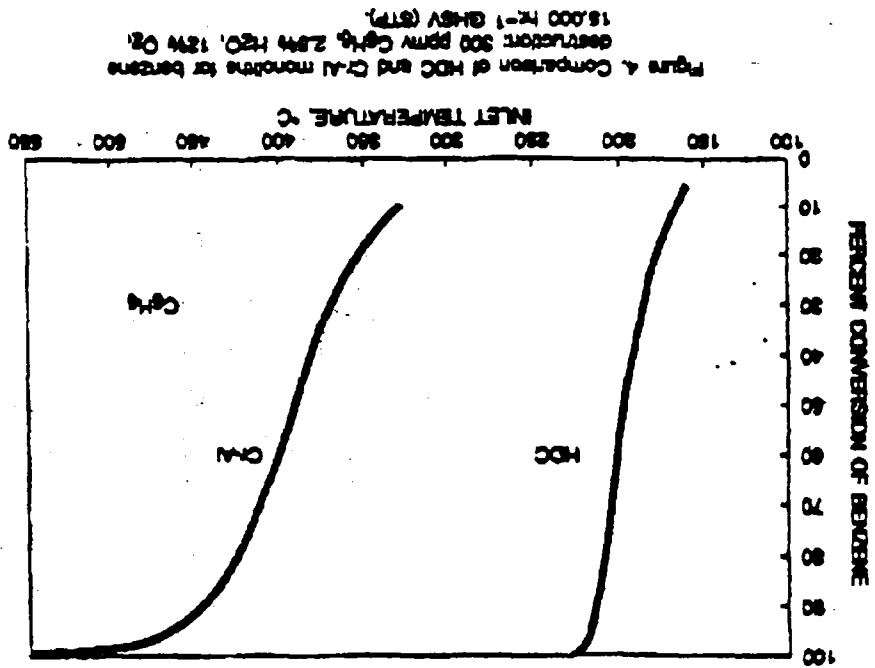
Although a large number of base and noble metal catalysts have been evaluated for the destruction of halogenated volatile organic compounds,<sup>4-14</sup> chromia-aluminas (typically 12-25 w.% chromia calculated as Cr<sub>2</sub>O<sub>3</sub>) seem to have been used most broadly and successfully.

Manning<sup>4</sup> studied the kinetics of destruction of methylene chloride (CH<sub>2</sub>Cl<sub>2</sub>) and several polychlorinated ethylenes in moistened air with a recycle reactor containing a commercially available 12 w.% Cr<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub> (0.40 cm x 0.40 cm pellets, Stream 34-0200). He concluded that the reaction was first order in the chlorohydrocarbon (except half order for trichloroethylene (C<sub>2</sub>HCl<sub>3</sub>)) and between zero and first order in oxygen. The reaction was slightly inhibited by water for all of the chlorohydrocarbons except perchloroethylene (C<sub>2</sub>Cl<sub>4</sub>). However, the presence of water improved the catalyst stability; it was suggested that the water inhibited the loss of Cr from the reactor, which presumably occurred as a result of the reaction of Cr<sub>2</sub>O<sub>3</sub> with the chlorohydrocarbon (or with the oxidation product Cl<sub>2</sub>) to produce the volatile red oxychloride, CrO<sub>2</sub>Cl<sub>2</sub>.

Weldon and Senkan<sup>11</sup> reported a kinetic study of the destruction of methylenchloride (CH<sub>2</sub>Cl<sub>2</sub>) with a powder (1 mm diameter) crushed from another commercially available Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> (1/8" Pellets, 19 w.% as Cr<sub>2</sub>O<sub>3</sub>, Harshaw). They also concluded that the reaction was first order (or perhaps non-linear second order) in the chlorohydrocarbon and zero order in O<sub>2</sub>. Because their reaction gases were dry (except for product H<sub>2</sub>O), they found selectivity to Cl<sub>2</sub> (relative to HCl) of 8-7 percent; this was significantly less than would correspond to the full Deacon equilibrium ( $4 \text{ HCl} + \text{O}_2 \rightleftharpoons 2 \text{Cl}_2 + 2 \text{H}_2\text{O}$ ), which would be in the range of 15-50 percent for their conditions. By contrast, Leidig<sup>5</sup> had found selectivities of 19-43 percent Cl<sub>2</sub> using copper-based catalysts. The difference probably reflects the significant difference in the relative efficacy of Cr and Cu for the Deacon reaction.

The research group at the University of Bath<sup>6</sup> which is seeking to develop a process for the catalytic combustion of polychlorinated biphenyls has measured the efficiency of destruction of 1,2,4-trichlorobenzene with packed beds of either 20 w.% Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> or 0.8 w.% Pt-Al<sub>2</sub>O<sub>3</sub> in 3.2 mm cylindrical pellets at 500-800 °C at air-fuel stoichiometry and with 25% excess air. At least 800 °C was required to achieve 90% conversion with either catalyst, but the Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> was more active in the range of 500-800 °C.





Chromia-alumina is the only catalyst composition identified in the patent<sup>12</sup> describing the fluidized-bed catalytic incinerator process of Air Resources, Inc. (ARI) which is reported to be in commercial use for the destruction of chlorinated organics.<sup>1</sup> The catalyzed bed in this process is fluidized (or, more accurately, agitated by up-flowing air) in an effort to counter the suppression of activity by chlorine (or chloride); it is intended that the continuous abrasion and loss from the reactor of the chlorine-laden outer portion of the catalyst particles will continuously expose unpoisoned particles to the reactants. To this end, the physical properties of the catalyst are adjusted to achieve a loss of about one pound of catalyst per million cubic feet of gas treated, or about 16 mg/m<sup>3</sup>. A skid-mounted ARI pilot plant, presumably loaded with chromia-alumina spheres per the ARI patent, was used by Radian Corporation under an EPA/Air Force contract in an extensive study of the catalytic destruction of a number of chlorinated organics and hydrocarbons such as might be impurities in the exhaust air from air strippers used to clean up contaminated soil or groundwater.<sup>13,17</sup> This unit demonstrated 97-99% destruction of the selected mixtures of chlorinated organics at a space velocity of about 7000 hr<sup>-1</sup> (STP) and 500°C. The chlorinated organics included vinyl chloride and polychlorinated ethanes and ethylenes.

Although noble metal catalysts have been studied for these reactions<sup>14,15,16</sup>, their performance has generally been inferior to the chromia-alumina, presumably because of the inhibition of the rate by the reactant chlorinated hydrocarbon and/or by the chromia/chloride products.<sup>18</sup> For example, a study,<sup>14</sup> similar otherwise to the chromia-alumina Radian/EPA/AF tests referred to above,<sup>13,17</sup> with an Engelhard Pt/Pd honeycomb catalyst reported destruction efficiencies of less than 50% for similar mixtures of chlorinated hydrocarbons which were destroyed at 97-99% efficiency by the fluidized base metal catalyst.

#### Results from this study

**Comparison of HDC with Cr<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>.** In order to compare the new Allied-Signal halo-hydrocarbon destruction catalyst (HDC) with the pre-existing catalyst technology, a chromia-alumina catalyst (19.7 w.% Cr<sub>2</sub>O<sub>3</sub> on Al<sub>2</sub>O<sub>3</sub>, 125 m<sup>2</sup>/g) was obtained from Harshaw Chemical Co. and applied as a washcoat to a Corning 400 cells/in<sup>2</sup> monolithic catalyst support by a conventional method.<sup>19</sup> Cores of this catalyst (Cr-Al, 7/8" diameter and 1" long) were tested along side similar size units of the experimental HDC, which were also prepared on the 400 cells/in<sup>2</sup> Corning cordierite support.

Figure 8 shows conversion-temperature curves for the HDC and Cr-Al monoliths for the destruction of carbon tetrachloride (CCl<sub>4</sub>), tested at 1000 volume ppm at 15,000 hr<sup>-1</sup> GHSV (STP) in N<sub>2</sub> containing 12% O<sub>2</sub> and 10% H<sub>2</sub>O. Over 99% destruction was achieved at about 385°C for the HDC, which was 200°C lower than was required by the Cr-Al reference catalyst. The difference in efficiency is even more pronounced for benzene (Figure 4) which required 225°C for 99% destruction with the HDC, and 490°C for the Cr-Al catalyst. For this comparison, the benzene level was 800 volume ppm (ppmv), and H<sub>2</sub>O level was 2.5%. Figure 8 shows that the activity difference is less for toluene, but that the HDC still gives 99% destruction at a lower temperature than the Cr-Al catalyst by 150°C (230°C vs. 380°C).

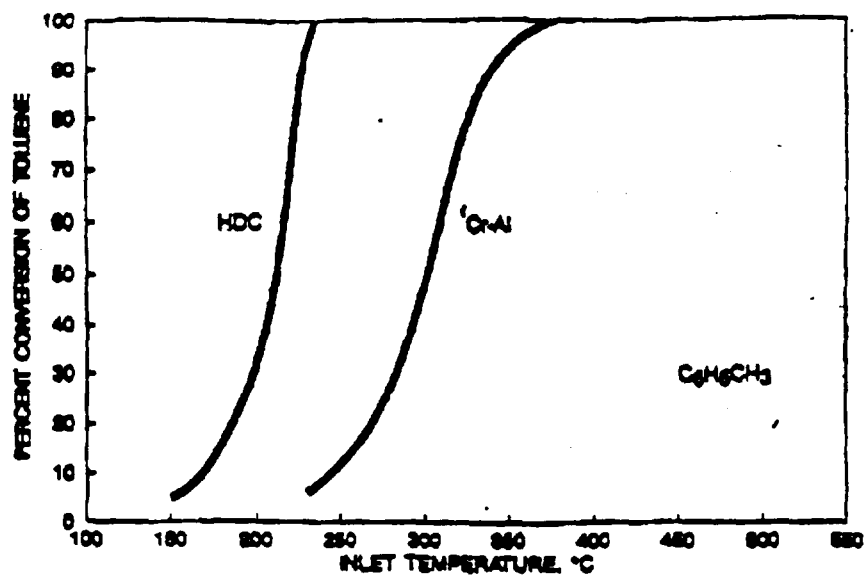


Figure 5. Comparison of HDC and Cr-Al monoliths for toluene destruction: 300 ppmv  $C_6H_5$ , 2.5%  $H_2O$ , 12%  $O_2$ , 15,000  $hr^{-1}$  GHSV (STP).

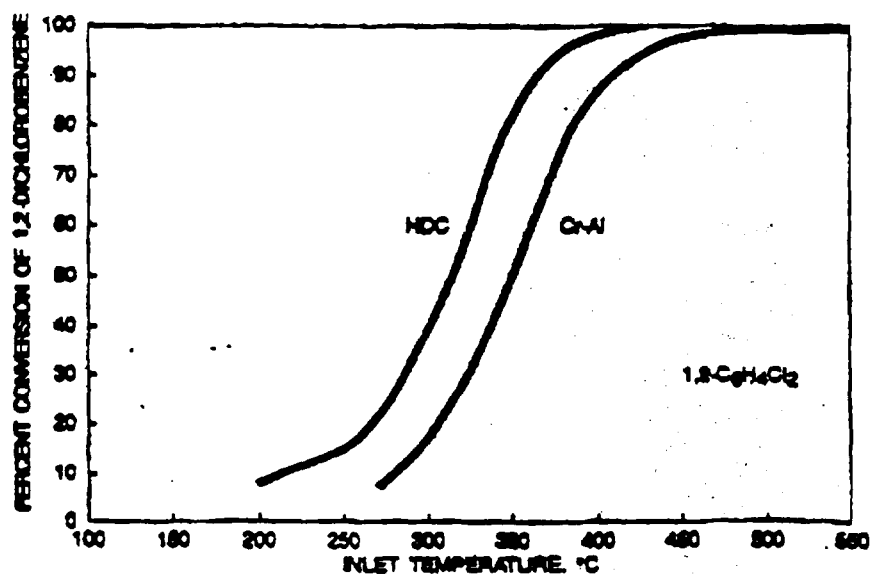


Figure 6. Comparison of HDC and Cr-Al monoliths for 1,2-dichlorobenzene destruction: 30 ppmv  $C_6H_4Cl_2$ , 2.5%  $H_2O$ , 12%  $O_2$ , 15,000  $hr^{-1}$  GHSV (STP).

The relative efficiency of the two catalysts for 1,2-dichlorobenzene at 80 ppmv is shown in Figure 6. Although this halogenated hydrocarbon is difficult for both catalysts, 99% destruction is achieved by the DHC at 405°C as compared to 500°C for Cr-Al. In this temperature range, the ability to operate at lower temperatures may have a major impact on catalyst stability, beyond the obvious fuel savings which result from the lower temperature operation.

The results shown in these figures for the Cr-Al monolithic catalyst are not unexpected in view of what might have been expected by extrapolation of the literature results for such catalyst in packed beds and fluidized systems. The considerably better performance of the Allied-Signal HDC compared to Cr-Al suggests that it might be usable in fixed bed processes at much lower temperatures than Cr-Al, without the problems associated with fluidized bed operation, including the emission of fine halogen-laden catalyst particulates, or the provision for trapping and collection of such potentially hazardous particulates.

Parametric studies with the Allied-Signal HDC. The effect of water concentration on carbon tetrachloride destruction by the new catalyst is shown in Figure 7, where the destruction efficiency is shown to decrease as the water level is increased from 1.5 to 10 volume percent. This slight inhibition by water in this concentration range probably reflects the competition of the reactant  $\text{CCl}_4$  with  $\text{H}_2\text{O}$  for adsorption at the catalyst site, and indicates the importance of the water concentration, and perhaps the  $\text{H}_2\text{O}$ :chlorohydrocarbon ratio in the feed gas.

The stability of the HDC at these operating conditions is also shown in Figure 7. At each water level, the catalysts were operated with the test gas at 375°C for over 48 hours and then retested; the curves for the retest were not distinguishable from the initial tests at either water level. The test at the 10%  $\text{H}_2\text{O}$  level was continued through 1800 hours, after which the conversion at 350°C was still above 99%; during the 1800-hour test, the benzene conversion-temperature profile actually shifted slightly to lower temperatures, reflecting an improvement in activity for  $\text{C}_6\text{H}_6$  destruction. In a parallel test, it was demonstrated that destruction of  $\text{CCl}_4$  without water vapor in the feed caused catalyst deactivation and, of course, produced significant amounts of  $\text{Cl}_2$  instead of the  $\text{HCl}$  usually produced. This demonstrates the importance of water vapor in stabilizing the catalyst performance, and for producing the desired  $\text{HCl}$  rather than  $\text{Cl}_2$ .

Figure 8 includes plots of the destruction of 1,1,2-trichloroethane ( $\text{Cl}_2\text{HC}-\text{CH}_2\text{Cl}$ ) at 450 ppmv and at two gas flow rates. At the 99% conversion level, operation at the lower flow rate (7500  $\text{hr}^{-1}$  GHSV (STP)) requires only 400°C instead of the 440°C required at the higher rate.

A somewhat negative order of the reaction with respect to the 1,1,2-trichloroethane is indicated in Figure 8. The nine-fold increase in halogenated organic from 50 to 450 ppm increases the temperature required for 99% conversion from 360°C to 400°C required at the higher rate.

The new halohydrocarbon destruction catalyst can also be prepared as an extrudate, granules, or in pellet forms for use in fixed bed reactors. Figure 10 shows results for  $\text{CCl}_4$  with the catalyst in the form of 1/16" extrudates at two different gas flow rates;

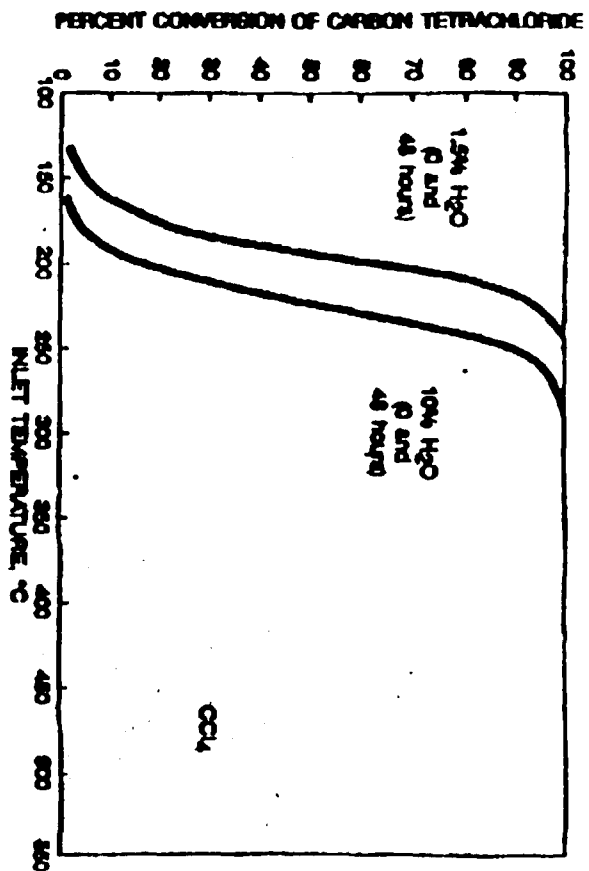


Figure 7. Destruction of carbon tetrachloride over monolithic H<sub>2</sub>O at 1.5 and 10% H<sub>2</sub>O levels: 1000 ppmv CCl<sub>4</sub> in air at 16,000 hr<sup>-1</sup> GHSV (STP), 1.5 or 10 volume % H<sub>2</sub>O.

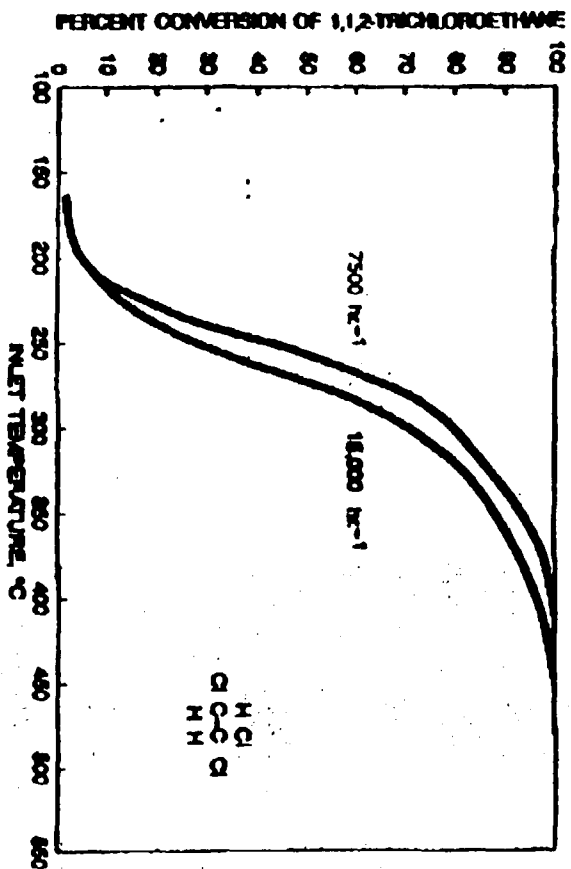


Figure 8. Destruction of 1,1,2-trichloroethane over monolithic H<sub>2</sub>O at two gas throughput rates: 1.5% H<sub>2</sub>O in air at 7500 and 16,000 hr<sup>-1</sup> GHSV (STP), 480 ppmv C<sub>2</sub>H<sub>3</sub>Cl<sub>3</sub>.

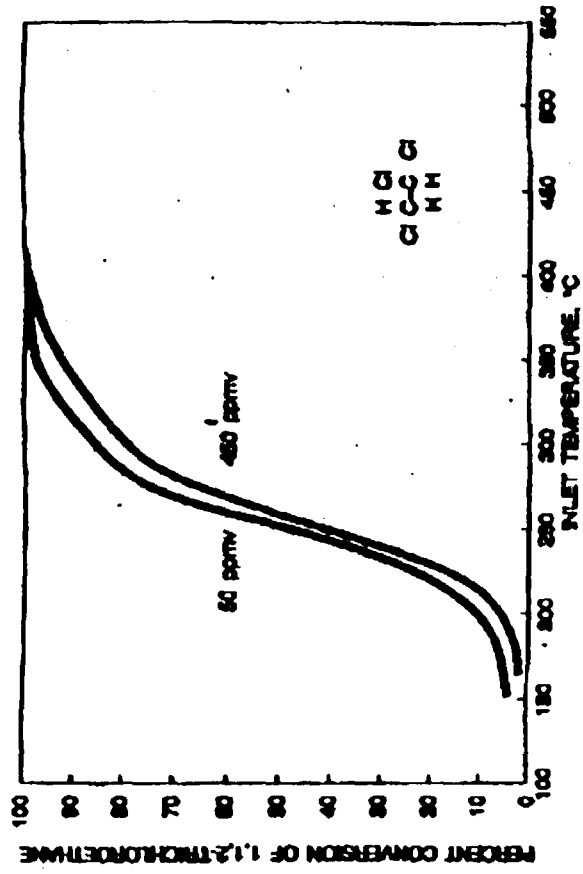


Figure 9. Destruction of 1,1,2-trichloroethane over monochloric HOC at two  $\text{C}_2\text{H}_5\text{Cl}$  concentrations: 1.5%  $\text{H}_2\text{O}$  in air at 7500  $\text{hr}^{-1}$  GHSV (STP).

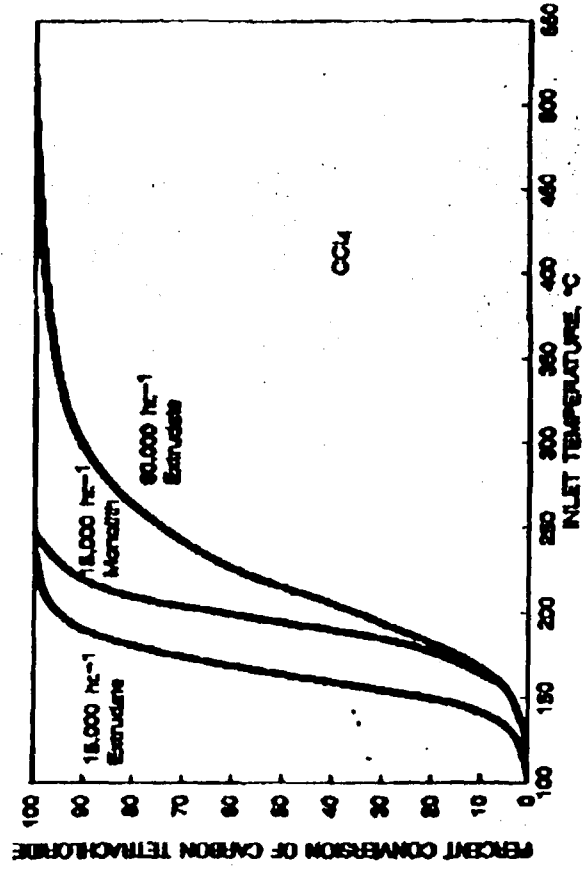


Figure 10. Destruction of carbon tetrachloride by bed of 1/16-inch HOC adsorbent at two space velocities and monochloric HOC at 18,000  $\text{hr}^{-1}$  GHSV (STP): 1.5%  $\text{H}_2\text{O}$  in air, 1000 ppmv  $\text{CCl}_4$ .

the plot for the 400 cells/in<sup>2</sup> monolithic catalyst is also shown for comparison. It is obvious that the extrudate bed gives somewhat better performance than the monolith at the same flow rate, but the back pressure is, of course, much greater in the extrudate bed.

The relative ease of destruction of the chloromethanes by the HDC is shown in Figure 11, at concentrations of 500-900 ppmv. The ease of destruction as shown increases monotonically from CH<sub>3</sub>Cl (most difficult) to CCl<sub>4</sub> (easiest) as the number of chlorine atoms increases; this in spite of an increasing actual Cl atom concentration across the series from 600 ppm (Cl atom) for CH<sub>3</sub>Cl to 3,600 ppm (Cl atom) for CCl<sub>4</sub>. The observed order of stability is in the same order as the lowest bond dissociation energies (LEDE's<sup>10</sup>), but is opposite to that found by Bond and Sadeghi for destruction of the polychloromethanes with several Pt-Al<sub>2</sub>O<sub>3</sub> catalysts.<sup>11</sup> The LEDE's and the temperatures required to achieve 99% destruction with the HDC catalyst are tabulated here, along with the temperature required to achieve 99% destruction by thermal oxidation, as reported by Taylor and Dellinger.<sup>12</sup> The EPA<sup>13</sup> has ranked these compounds from the most difficult to the least difficult to incinerate thermally as: CCl<sub>4</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl, CH<sub>3</sub>CH<sub>2</sub>Cl.<sup>13</sup>

Lowest Bond Dissociation Energies (LEDE<sup>10</sup>) and the Temperatures Required to Achieve 99% Destruction Efficiency (D.E.) by Thermal<sup>12</sup> Oxidation, and by Catalytic Oxidation with HDC.

	LEDE kcal/ mole	T-99%, Thermal	T-99%, HDC
CH <sub>3</sub> Cl	83.5	805°C	> 850°C
CH <sub>2</sub> Cl <sub>2</sub>	79.0	755	491
CHCl <sub>3</sub>	77.0	695	397
CCl <sub>4</sub>	70.4	750	240

It is clear that the relative ease of breaking the weakest chlorocarbon bond correlates well with the relative ease of destruction by the HDC, and is probably the factor which determines the relative ease of destruction. This is, of course, obviously not the determining factor in their destruction over the Pt-Al<sub>2</sub>O<sub>3</sub> catalyst of Bond and Sadeghi.<sup>11</sup>

The slightly easier destruction of some fluorinated hydrocarbons relative to their chlorinated analogues (over the new HDC) is illustrated in Figure 12; the temperatures required for 99% conversion are 280°C and 320°C for fluorobenzene and chlorobenzene, respectively at these conditions. Similarly, 1,2-difluoroethane and 1,2-dichloroethane were found to give very similar conversion-temperature curves over the HDC, as illustrated for the former in Figure 18. That figure also shows the greater ease of catalytic destruction of the geminal dihaloethanes (1,1-difluoroethane) relative to the vicinal compound (1,2-difluoroethane). This difference is also consistent with a greater ease of destruction by the HDC of the compound with a weaker halocarbon bond as was found for the series of chloromethanes (Figure 11).

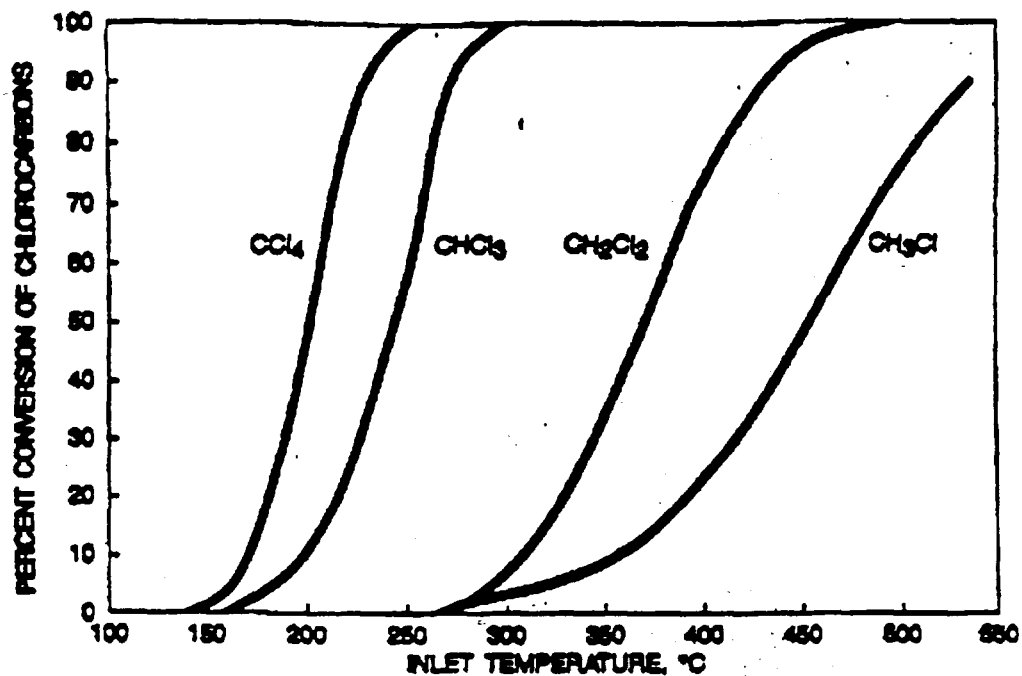


Figure 11. Destruction of the C-1 chlorocarbons over  
HDC: 1.5% H<sub>2</sub>O in air at 15,000 hr<sup>-1</sup> GHSV (STP).  
Chlorocarbon concentrations: CCl<sub>4</sub>-500 ppmv;  
CHCl<sub>3</sub>-500 ppmv, CH<sub>2</sub>Cl<sub>2</sub>-500 ppmv, CH<sub>3</sub>Cl-500 ppmv.



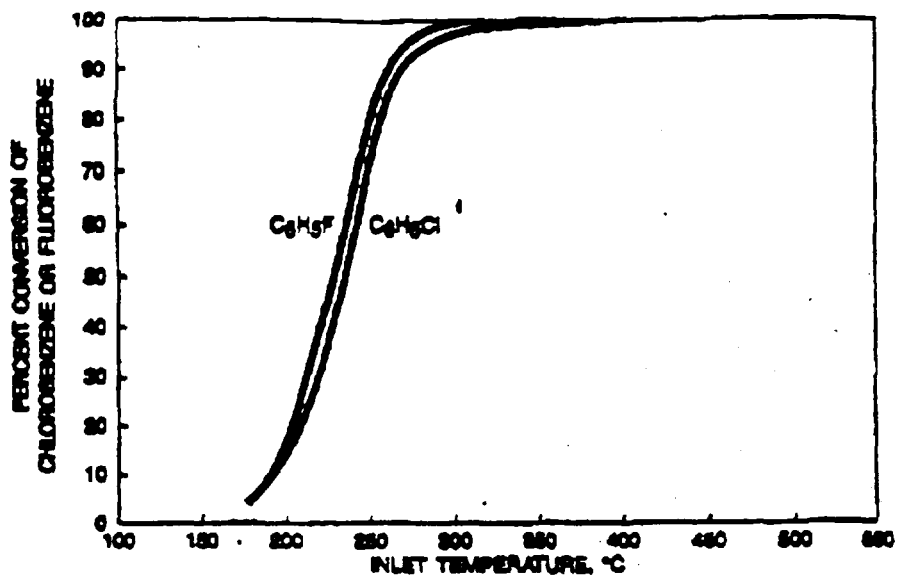


Figure 12. Destruction of chlorobenzene and fluorobenzene over monolithic HOC: 8.8%  $H_2O$ , 12%  $O_2$ , at  $15,000 \text{ hr}^{-1}$  GHSV (STP), 100 ppmv of  $C_6H_5Cl$  or  $C_6H_5F$ .

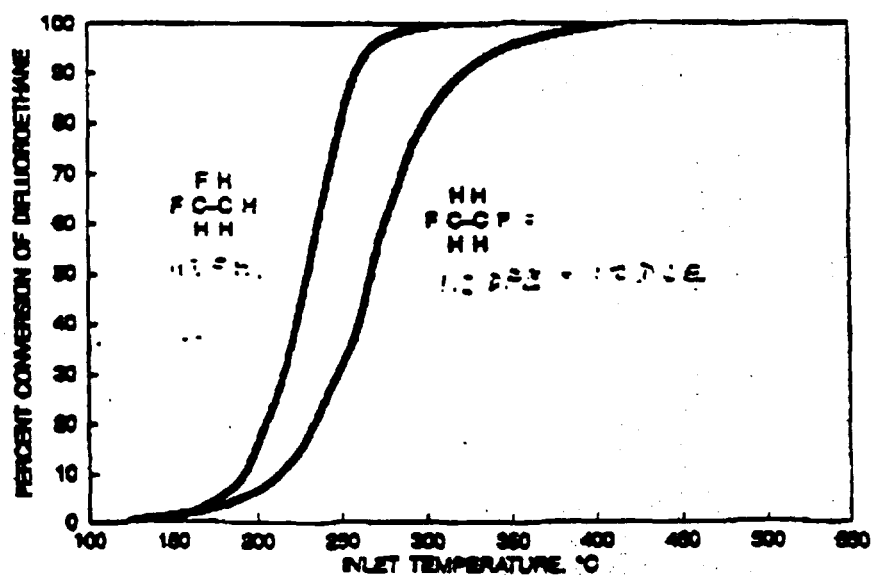


Figure 13. Destruction of 1,1-difluoroethane and of 1,2-difluoroethane over monolithic HOC: 1.8%  $H_2O$  in air at  $15,000 \text{ hr}^{-1}$  GHSV (STP), 400 ppmv of  $C_2H_4F_2$ .

## CONCLUSION

Results have been presented for the destruction of a number of diverse chlorinated and fluorinated hydrocarbons over a monolithic or particulate form of a new proprietary catalyst, referred to as a halohydrocarbon destruction catalyst (HDC). The HDC appears to be significantly more active, stable, and insensitive to inhibition by halogen, than the supported noble metal or chromia-alumina catalysts previously described. The relative ease of destruction of a particular series of halohydrocarbon over the new Allied-Signal halohydrocarbon destruction catalyst appears to be determined by the bond dissociation energy of the weakest halocarbon bonds in the halohydrocarbon, rather than being inversely proportioned to the number of halogen atoms per molecule.

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